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Spectrophotometric method for the selective determination of catechol

Anjali Pal

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302

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A simple, accurate and selective method for catechol determination has been developed. The method is based on the oxidation of catechol by silver carbonate adsorbed on celite known as Fetizon's reagent in toluene medium at room temperature followed by its treatment with triethanolamine. This causes development of a bright red colour. The coloured solution thus produced has absorption maxima at 501 nm (molar absorptivity, $\varepsilon = 2.33 \times 10^3$ litre mol^{-1} cm^{-1}) and 322 nm (molar absorptivity, $\varepsilon = 9.13 \times 10^4$ litre mol^{-1} cm^{-1}). Calibration curves at the two different wavelengths obey Beer's law in the concentration range 0-52 ppm of catechol. The correlation coefficients are 0.995 and 0.994 respectively. The relative standard deviation is found to be less than 5%. The Sandell sensitivities with respect to catechol concentration are 4.721×10^{-2} μg cm^{-2} at 501 nm and 1.204×10^{-3} μg cm^{-2} at 322 nm. The effect of reagent concentration, solvent and reaction time etc. are discussed. The method has been applied for the quantification of catechol in water.

Phenols have tremendous chemical and biological importance and can be detected and determined following various methods. But most of the methods lack selectivity for individual members of the family. Catechol being one such member is important due to the fact that it can act as amino acid inhibitor[1], neuromuscular transmitter[2], convulsant agent[3], synaptic transmitter[4], carcinogen[5] and is a well known toxic metabolite[6]. It occurs in tobacco smoke[7] and acts as a benzene metabolite[8] and also as a precursor of melanin, lignins and insect scleroproteins. Chemical products derived from the purified catechol include pharmaceuticals, flavours, agrochemicals and polymerisation inhibitors and antioxidants. Thus a selective method for the detection and quantification of catechol is an important aspect of analytical chemistry.

A commonly used method for phenolic compound determination utilises the colour reaction with 4-amino antipyrine[9] and is applicable but not selective for catechol. Another method for phenol quantification is based on the coupling reactions of phenols with diazonium salts[10]. This procedure can also be used for catechol but is also nonspecific. Some specific known chemical methods for catechol determination involve reactions with sodalime[11], phloroglucinol[12] and nitrite[13] and physical methods include chromatography[7], polarography[14] and titrimetry[15].

Herein we report a new selective method for the determination of catechol involving a two step process. The first step involves the oxidation of catechol in toluene using Fetizen's reagent[16] (silver carbonate adsorbed on celite) to give the corresponding quinone. The oxidising agents so far used for this purpose are MnO_4^-, $Fe(CN)_6^{-3}$, Fe(III), OCl^-, chloramine-T, H_2O_2, IO_4^-[17] etc, most of which are *p*H sensitive and condition dependent. The second step involves the treatment of the solution with triethanolamine (TEA) and acetonitrile (CH_3CN) to produce colour (λ_{max} = 501 and 322 nm). The absorbance values at both absorption maxima are direct measure of catechol concentration.

Materials and Methods

All chemicals and solvents used were of AR grade and the water used was double distilled. Catechol (SD Chemical) was doubly crystallised from ethyl acetate-pet. ether and the purity was tested through TLC and melting point determination. Toluene solution of catechol was stored in the refrigerator for one week and the water solution prepared daily. The oxidising agent Ag_2CO_3-celite was prepared according to the literature procedure[16].

All absorbance measurements were done with a Shimadzu Model UV-160 digital Spectrophotometer (Kyoto, Japan).

Standard procedure for the determination of catechol concentration in toluene

To a series of 10 mL solution of catechol in toluene having different concentrations ranging from

1-104 ppm, 60-70 mg portions of Ag_2CO_3-celite were added and stirred magnetically at room temperature for 1 hr. The reaction mixtures were then allowed to settle for 10 min. Then, 2 mL portions of clear toluene solution from each was mixed with 0.2 mL of TEA (1 : 1 v/v mixture with CH_3CN) when a red complex separated. This was insoluble in toluene and made soluble by adding 1.8 mL CH_3CN. It gave rise to a red homogeneous solution having two different absorption maxima at 501 and 322 nm. The final catechol concentration ranged from 0.5-52 ppm. The colour was stable for more than 3 hr. Two calibration curves were prepared at different absorption maxima.

Results and Discussion

Oxidation of catechol by Ag_2CO_3-celite and formation of colour thereafter with TEA

Oxidation of phenolic compounds by Ag_2CO_3-celite in organic solvent such as benzene, is known[16] in synthetic organic chemistry as a convenient route for producing an oxidatively coupled product or a quinone depending on the substrate. Quinone formation by other oxidising agents such as MnO_4^-, $Fe(CN)_6^{-3}$, Fe(III), OCl^-, chloramine-T, H_2O_2, IO_4^- etc. are possible but are sensitive towards condition. The advantage in our procedure is that the reagent is very mild so that many phenolic compounds do not form the quinonoid compound. Since the reagent is a solid it is easily separable from the reaction mixture by decantation. The reagent is very stable and can be stored for months.

The absorption spectra of the quinonoid product before addition of TEA is shown in Figure 1 (dashed line). The absorption spectrum (Fig. 1, curve-A) of the red coloured solution after treating the quinone with TEA and CH_3CN shows characteristic maxima at 501 and 322 nm respectively, whereas the blank (curve-B) does not show any absorption at these wavelengths. It is observed that other organic bases such as aniline, triethylamine, and N,N-dimethylaniline did not form any colour. Acetonitrile is used because it solubilises the complex easily and in this solvent the colour remains stable.

Effect of reagent concentration

Experimental results show that in the range of catechol used (10-1040 μg), ~ 60 mg of the reagent is sufficient, however, higher amounts (~ 100 mg) did not hamper the determination. So 60-70 mg reagent was used for each reaction.

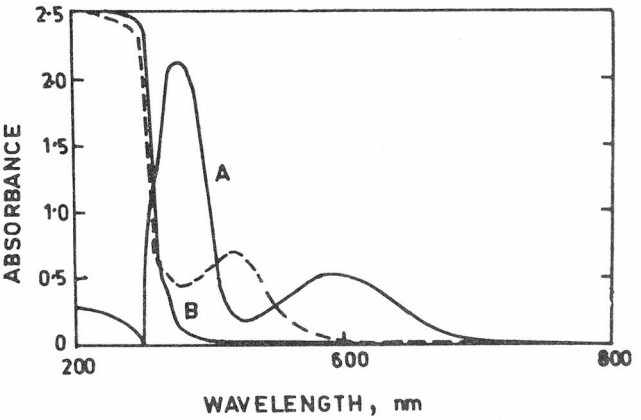

Figure 1—Absorption spectra of the oxidation product of catechol (conc. 51.80 ppm) by Fetizon's reagent before (---; ref : air) and after (A; ref : reagent blank) treatment with TEA & CH_3CN. Curve-B is the absorption spectra of the reagent blank (ref : air)

Effect of reaction time

To ascertain the time needed for oxidation a kinetic study was made. It was found that 60-70 min. stirring was optimum for the oxidation. However, kinetics for two different peaks are different. The peak in the UV-region attains maximum absorbance value in a much faster rate than that in VIS-region. Thus, the two peaks are presumably due to two different compounds.

Effect of TEA concentration

Since the red colour develops only after the addition of TEA, it is important to find out the TEA concentration required for optimum colour generation. It was observed that 160-240 μL TEA (1 : 1 v/v mixture with CH_3CN) in the described working range of catechol was optimum. Lower amounts caused decrease in the peak intensity. Hence 200 μL portions of TEA was used in each case.

Choice of solvent

Solvent plays an important role in this reaction. A number of solvents were tried as the medium for the oxidation reaction and was followed by the addition of TEA in CH_3CN. The solvents tried for oxidation were benzene, toluene, cyclohexane, ethyl acetate, diethyl ether, CH_3CN, methanol and water. Among these, EtOAc and Et_2O could produce red colour with much less intensity. In CH_3CN and MeOH colloidal solutions were produced in the oxidation step and so they were avoided. No colour could be obtained in cyclohexane and H_2O. Benzene and toluene worked best but benzene was avoided due to

health hazards and therefore, toluene was used throughout the study.

Calibration graph and other statistical parameters

A series of toluene solutions of catechol were oxidised with Ag_2CO_3-celite and then treated with TEA/CH_3CN to generate a red solution with λ_{max} 501 and 322 nm. The concentration ranged from 0-52 ppm. Two separate calibration curves were prepared at two different wavelengths. Beer's law was obeyed for both. Linear regression performed over the linear response region provided correlation coefficients 0.995 (at 501 nm) and 0.994 (at 322 nm) with the intercepts of -0.0051 and -0.0128 and slopes of 1.02×10^{-2} and 4.2×10^{-2} ppm^{-1} respectively. It was observed that a distinct red colour could be seen with 1 ppm of catechol and with 0.5 ppm catechol absorbance at 322 nm could easily be seen. The molar absorptivities were 2.33×10^3 litre $mol^{-1}\,cm^{-1}$ (at 501 nm) and 9.13×10^4 litre $mol^{-1}\,cm^{-1}$ (at 322 nm). The relative standard deviation for all measurements were < 5%. The Sandell sensitivities with respect to catechol were 4.721×10^{-2} $\mu g\ cm^{-2}$ (at 501 nm) and 1.204×10^{-3} $\mu g\,cm^{-2}$ (at 322 nm).

Interferences

The following hydroxy compounds (5 mg each/10 mL toluene) viz. phenol, resorcinol, 2-naphthol, 1-naphthol, 3-aminophenol, 4-aminophenol, 2,3-dihydroxynaphthalene, 4-*t*-butylcatechol, vanilline, pyrogallol, gallic acid and 3-(3,4-dihydroxyphenyl) alanine (DOPA) did not give the colouration under the procedure discussed. Hydroquinone, however, under similar conditions produced slight red colour only after long time.

Determination of catechol concentration in water

The method when coupled to a suitable extraction step can sucessfully be applied for the analysis of catechol in water samples. The extraction also helps preconcentration of catechol from the water and thus higher sensitivity could be achieved.

A known volume of the spiked water with known concentration of catechol was first made acidic with conc. HCl (*p*H 1). The analyte was then extracted with EtOAc (known volume)[19,20]. Preconcentration in this step can easily be achieved upto 10 fold or more. The extract with a suitable volume was then evaporated to dryness, first on a water-bath and then by a vacuum drier. This was mixed with toluene (10 mL) and then the usual procedure for oxidation and subsequent colour development with TEA was followed. The absorbances at 501 and 322 nm were measured. During mixing of toluene also, preconcentration is possible. The concentrations determined by using the pre-established calibration curves and the absorbances obtained by this procedure are given in Table I.

Conclusion

The present paper describes a simple and selective spectrophotomeric method for the quantification of catechol. It is based on two steps: first step is the oxidation of catechol by silver carbonate supported on celite. Supported reagents has the advantage of being removed from the reaction medium easily. It also manifests a selectivity which is not present with corresponding solution systems. It is efficient because of its large surface area. The second step is the complexation of the oxidised product with triethanolamine to a red product. Possibly this is a donor-acceptor type of complex. The appearance of two absorption maxima is possibly due to two different compounds. Catechol analysis in water sample is possible using this method.

Table I—Analysis of water sample

Sample No.	Volume (mL) taken/used for			Concentration of catechol (ppm) present in the parent spiked sample	Concentration of catechol (ppm) found* for the parent spiked sample using absorbance values at λ_{max}	
	the spiked sample	the extraction	the evaporation		501 nm	322 nm
1	20	10	7	38.7	34.1	34.8
2	10	10	2	387.0	341.2	432.1

*Accuracy ± 12%

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References

1 Shikimi T, Inagaki C & Takauri S, *Experientia*, 34, **1978**, 1188.
2 Blaber L C & Callagher J P, *Neuropharmacology*, 10, **1971**, 151.
3 Angel A, Clarns K A & Dowhurst D C, *Br J Pharmacol*, 61, **1977**, 433.
4 Heckman J C, Ross D B & Davidoff R A, *Brain Res*, 157, **1970**, 47.
5 Walters D B, Chamberlain D J, Akin F J, Snook M E & Chortyk O T, *Anal Chim Acta*, 99, **1978**, 143.
6 Irons R D & Neptun D A, *Toxicol*, 45, **1980**, 297.
7 Risner C H & Cash S L, *J Chromatogr Sci*, 28, **1990**, 239.
8 Greenlee W P, Chism J P & Rickert D E, *Analyt Biochem*, 112, **1981**, 367.
9 Lacoste R J, Venable S H & Stone J C, *Analyt Chem*, 31, **1959**, 1246.
10 Rayburn C H, Harlan W R & Hanmer H R, *Analyt Chem*, 25, **1953**, 1419.
11 Shamsuddin K M, Ali S & Qureshi P M, *Talanta*, 38, **1991**, 1041.
12 Qureshi M, Shamsuddin K M, Ali S, Qureshi P M, Iqbal S & Mamoonpuri M, *Analyt Lett*, 22, **1989**, 2359.
13 Waite J H & Tanzer M L, *Analyt Biochem*, 111, **1981**, 131.
14 Tur'yan I Ya, Il'ina L F, Kudinov P I & Kochubei N D, *Zh Anal Khim*, 30, **1975**, 1842.
15 Amin D & Sulaiman S T, *Analyst*, 109, **1984**, 739.
16 Balogh V, Fetizon M & Golfier M, *J Org Chem*, 36, **1971**, 1339.
17 Sastry C S, Das V G & Rao K E, *Analyst*, 110, **1985**, 395.
18 Fetizon M, Golfier M, Mourgues P & Louis J M, *Organic synthesis by oxidation with metal compounds*, edited by W J Mijs & C R H I De Jonge (Plenum Press, N Y), **1986**, p.560.
19 Nowicka-Jankowska T, Gorczynska K, Michalik A & Wieteska E, *Comprehensive analytical chemistry*, edited by G Svehla, (Elsevier Science Publishers, B V), **1986**, p.579.
20 Pal A, *Bull Chem Soc Japan*, 67, **1994**, 2420.